

## Freeform Search

<b>Database:</b>	US Pre-Grant Publication Full-Text Database US Patents Full-Text Database US OCR Full-Text Database EPO Abstracts Database JPO Abstracts Database Derwent World Patents Index IBM Technical Disclosure Bulletins
<b>Term:</b>	"nf-90"
<b>Display:</b>	10 Documents in <b>Display Format:</b> CIT <b>Starting with Number</b> 1
<b>Generate:</b> <input type="radio"/> Hit List <input checked="" type="radio"/> Hit Count <input type="radio"/> Side by Side <input type="radio"/> Image	

### Search History

DATE: Monday, June 06, 2005    [Printable Copy](#)    [Create Case](#)

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DB=USPT; PLUR=YES; OP=ADJ			
<u>L26</u>	"nf-90"	5	<u>L26</u>
<u>L25</u>	refining same potable water and nanofiltration	0	<u>L25</u>
<u>L24</u>	L23 and potable water	3	<u>L24</u>
<u>L23</u>	L22 and nanofiltration	39	<u>L23</u>
<u>L22</u>	210/653.ccls.	202	<u>L22</u>
<u>L21</u>	l18 and nanofiltration and drinking water and softening	8	<u>L21</u>
<u>L20</u>	L19 and nf-90	0	<u>L20</u>
<u>L19</u>	L18 and water softening same nanofiltration	11	<u>L19</u>
<u>L18</u>	210/652.ccls.	478	<u>L18</u>
<u>L17</u>	water softening and polyamide same membrane and "nf-90"	0	<u>L17</u>
<u>L16</u>	L13 and nf same membrane	7	<u>L16</u>
<u>L15</u>	L14 and polyamide	1	<u>L15</u>
<u>L14</u>	L13 and potable water	3	<u>L14</u>
<u>L13</u>	L8 and nf same membrane	7	<u>L13</u>
<u>L12</u>	l8 and nanofiltratio	0	<u>L12</u>

<u>L11</u>	l8 and nf-90 and membrane	0	<u>L11</u>
<u>L10</u>	L9 and nanofiltration	1	<u>L10</u>
<u>L9</u>	L8 and drinking water and polyamide same membrane same composite	4	<u>L9</u>
<u>L8</u>	210/257.2.ccls.	441	<u>L8</u>
<u>L7</u>	L1 and film tec	2	<u>L7</u>
<u>L6</u>	L2 and film tec	0	<u>L6</u>
<u>L5</u>	l2 and "Film Tec"	0	<u>L5</u>
<u>L4</u>	L1 and "nf-90"	0	<u>L4</u>
<u>L3</u>	L2 and tfc	3	<u>L3</u>
<u>L2</u>	L1 and polyamide and support same polysulfone	49	<u>L2</u>
<u>L1</u>	membrane and composite and aromatic same piperazine	118	<u>L1</u>

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## Hit List

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Search Results - Record(s) 41 through 49 of 49 returned.

☐ 41. Document ID: US 4859384 A

L2: Entry 41 of 49

File: USPT

Aug 22, 1989

US-PAT-NO: 4859384

DOCUMENT-IDENTIFIER: US 4859384 A

**\*\* See image for Certificate of Correction \*\***

TITLE: Novel polyamide reverse osmosis membranes

DATE-ISSUED: August 22, 1989

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Fibiger; Richard F.	Midland	MI		
Koo; Ja-young	Plymouth	MN		
Forgach; David J.	Midland	MI		
Petersen; Robert J.	Minnesota	MN		
Schmidt; Donald L.	Midland	MI		
Wessling; Ritchie A.	Midland	MI		
Stocker; Thomas F.	St. Paul	MN		

US-CL-CURRENT: 264/45.1; 264/48, 264/DIG.48, 264/DIG.62

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KOOC	Draw De
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☐ 42. Document ID: US 4857363 A

L2: Entry 42 of 49

File: USPT

Aug 15, 1989

US-PAT-NO: 4857363

DOCUMENT-IDENTIFIER: US 4857363 A

**\*\* See image for Certificate of Correction \*\***

TITLE: Process for preparation of semipermeable composite membrane

DATE-ISSUED: August 15, 1989

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Sasaki; Tatsuo	Ohtsu			JP
Fujimaki; Hideo	Shiga			JP

Uemura; Tadahiro                      Kyoto                      JP  
Kurihara; Masaru                      Ohtsu                      JP

US-CL-CURRENT: 427/245; 427/340, 427/342

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWIC	Draw. D.
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☐ 43. Document ID: US 4830885 A

L2: Entry 43 of 49

File: USPT

May 16, 1989

US-PAT-NO: 4830885

DOCUMENT-IDENTIFIER: US 4830885 A

TITLE: Chlorine-resistant semipermeable membranes

DATE-ISSUED: May 16, 1989

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Tran; Chinh N.	San Diego	CA		
Chu; Hong C.	San Diego	CA		
Light; William G.	San Diego	CA		

US-CL-CURRENT: 427/245; 210/500.33, 210/500.37, 210/500.38, 210/500.41, 427/341,  
428/420

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWIC	Draw. D.
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☐ 44. Document ID: US 4812238 A

L2: Entry 44 of 49

File: USPT

Mar 14, 1989

US-PAT-NO: 4812238

DOCUMENT-IDENTIFIER: US 4812238 A

**\*\* See image for Certificate of Correction \*\***

TITLE: Membranes prepared via reaction of diazonium compounds or precursors

DATE-ISSUED: March 14, 1989

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Cadotte; John E.	Minnetonka	MN		
Schmidt; Donald L.	Midland	MI		

US-CL-CURRENT: 210/636; 210/500.3, 210/500.37, 210/500.38, 210/655

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWIC	Draw. D.
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☐ 45. Document ID: US 4769148 A

L2: Entry 45 of 49

File: USPT

Sep 6, 1988

US-PAT-NO: 4769148

DOCUMENT-IDENTIFIER: US 4769148 A

TITLE: Novel polyamide reverse osmosis membranes

DATE-ISSUED: September 6, 1988

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Fibiger; Richard F.	Midland	MI		
Koo; Ja-young	Plymouth	MN		
Forgach; David J.	Midland	MI		
Petersen; Robert J.	Minneapolis	MN		
Schmidt; Donald L.	Midland	MI		
Wessling; Ritchie A.	Midland	MI		
Stocker; Thomas F.	St. Paul	MN		

US-CL-CURRENT: 210/500.38; 528/312, 528/363

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KNIC	Draw D
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☐ 46. Document ID: US 4758343 A

L2: Entry 46 of 49

File: USPT

Jul 19, 1988

US-PAT-NO: 4758343

DOCUMENT-IDENTIFIER: US 4758343 A

**\*\* See image for Certificate of Correction \*\***TITLE: Interfacially synthesized reverse osmosis membrane

DATE-ISSUED: July 19, 1988

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Sasaki; Tatsuo	Ohtsu			JP
Fujimaki; Hideo	Shiga			JP
Uemura; Tadahiro	Kyoto			JP
Kurihara; Masaru	Ohtsu			JP

US-CL-CURRENT: 210/500.28; 210/500.38, 428/315.9, 428/420

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KNIC	Draw D
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☐ 47. Document ID: US 4659475 A

L2: Entry 47 of 49

File: USPT

Apr 21, 1987

US-PAT-NO: 4659475

DOCUMENT-IDENTIFIER: US 4659475 A

**\*\* See image for Certificate of Correction \*\***TITLE: Composite reverse osmosis membrane comprising crosslinked poly(amine-epihalohydrin adduct)

DATE-ISSUED: April 21, 1987

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Liao; Tsung K.	Kansas City	MO		
Chappelow; Cecil B.	Leawood	KS		

US-CL-CURRENT: 210/654; 210/500.37, 427/244

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KnowC	Draw De
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☐ 48. Document ID: US 4277344 A

L2: Entry 48 of 49

File: USPT

Jul 7, 1981

US-PAT-NO: 4277344

DOCUMENT-IDENTIFIER: US 4277344 A

**\*\* See image for Certificate of Correction \*\***TITLE: Interfacially synthesized reverse osmosis membrane

DATE-ISSUED: July 7, 1981

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Cadotte; John E.	Minnetonka	MN		

US-CL-CURRENT: 210/654; 210/490, 210/500.38, 427/243, 427/340, 428/420, 428/474.4, 428/475.2, 428/475.5, 428/475.8, 428/479.3, 428/543

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KnowC	Draw De
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☐ 49. Document ID: US 4259183 A

L2: Entry 49 of 49

File: USPT

Mar 31, 1981

US-PAT-NO: 4259183

DOCUMENT-IDENTIFIER: US 4259183 A

**\*\* See image for Certificate of Correction \*\***

TITLE: Reverse osmosis membrane

DATE-ISSUED: March 31, 1981

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Cadotte; John E.	Minnetonka	MN		

US-CL-CURRENT: 210/654; 210/500.28, 210/500.37, 210/500.38, 264/45.1, 427/246,  
525/344, 528/337

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	K00C	Draw De
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L1 and polyamide and support same polysulfone

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L16: Entry 3 of 7

File: USPT

Aug 15, 2000

DOCUMENT-IDENTIFIER: US 6103125 A

TITLE: Zero waste effluent water desalination system

Brief Summary Text (4):

It is known to purify (or treat) water through a variety of commercially available water treatment devices designed for point-of-use applications in the commercial/residential water treatment market. The most popular devices are based on the following technologies: activated carbon for organic removal: ultraviolet light disinfection: ion exchange for hardness removal (water softening), and membrane desalination such as reverse osmosis (RO) or nanofiltration (NF).

Brief Summary Text (5):

RO membranes have been used for desalination purposes for over two decades now. However, nanofiltration is relatively new in the field of water treatment technology. A NF membrane produces soft water by retaining the hardness creating, divalent ions present in water. A NF membrane allows a high percentage of monovalent ions such as sodium and chloride to pass through, while it retains a high percentage of the divalent ions. It is the monovalent ions that create osmotic pressure that requires the moderate to high pressures necessary to pump water through an RO membrane. Therefore, nanofilter membranes require much less pressure to pump water through the membrane because hydraulic driving force does not have to overcome the effect of osmotic pressure from monovalent ions. Generally speaking, RO membranes used for residential and commercial water treatment applications remove all dissolved solids by approximately 98%. while nanofilter membranes remove divalent ions (hardness components: calcium and magnesium) by approximately 90% and monovalent ions (sodium chloride) by approximately 50%.

Brief Summary Text (6):

Desalination devices that use membrane elements (for example: RO or NF) always create two streams of water as the water exits the element: desalinated product water (which has passed through the membrane), and a waste brine (that has flowed across the membrane surface). This waste brine stream is necessary to flush salts and minerals away from the membrane to prevent them from accumulating and fouling the membrane surface. If a buildup of salts and minerals in the feed-water to a membrane occurs continuously, dissolved substances can precipitate and form a solid film fouling the surface of the membrane. In addition, colloidal and particulate contaminants can also adhere to the membrane surface and cause fouling. With many water-borne contaminants, if a membrane becomes irreversibly scaled, or fouled, it can't be cleaned and must be replaced. This characteristic of membrane processes poses a significant problem in reducing waste effluent especially in point of use (POU) water treatment systems that are typically compact and built as economically as possible.

Current US Cross Reference Classification (3):210/257.2[Previous Doc](#)[Next Doc](#)[Go to Doc#](#)



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L19: Entry 11 of 11

File: USPT

May 28, 1996

DOCUMENT-IDENTIFIER: US 5520816 A

TITLE: Zero waste effluent desalination system

Detailed Description Text (26):

Another zero waste effluent softening system is shown in FIG. 3b. This is an unpumped version of the water softening system of FIG. 3a. Here, a membrane module 3, is placed in-line with the cold water service pipe. In this case, normal line pressure must be sufficient to produce softened water for the building. Softened water flows through the nanofiltration membrane contained in module 3, and is stored in tank 6, which feeds the hot water tank 7. The only controls necessary are a pressure switch 9, which opens valve 10, to allow unsoftened water to flow into the hot water heater tank 7, if the softening system cannot keep up with the demand.

Current US Cross Reference Classification (4):210/652[Previous Doc](#)[Next Doc](#)[Go to Doc#](#)

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L21: Entry 3 of 8

File: USPT

Jan 4, 2005

DOCUMENT-IDENTIFIER: US 6838001 B2

TITLE: Method of monitoring membrane separation processes

Brief Summary Text (4):

Membrane separation, which uses a selective membrane, is a fairly recent addition to the industrial separation technology for processing of liquid streams, such as water purification. In membrane separation, constituents of the influent typically pass through the membrane as a result of a driving force(s) in one effluent stream, thus leaving behind some portion of the original constituents in a second stream. Membrane separations commonly used for water purification or other liquid processing include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), electrodialysis, electrodeionization, pervaporation, membrane extraction, membrane distillation, membrane stripping, membrane aeration, and other processes. The driving force of the separation depends on the type of the membrane separation. Pressure-driven membrane filtration, also known as membrane filtration, includes microfiltration, ultrafiltration, nanofiltration and reverse osmosis, and uses pressure as a driving force, whereas the electrical driving force is used in electrodialysis and electrodeionization. Historically, membrane separation processes or systems were not considered cost effective for water treatment due to the adverse impacts that membrane scaling, membrane fouling, membrane degradation and the like had on the efficiency of removing solutes from aqueous water streams. However, advancements in technology have now made membrane separation a more commercially viable technology for treating aqueous feed streams suitable for use in industrial processes.

Brief Summary Text (7):

For example, monitoring techniques typically applied to reverse osmosis and nanofiltration include conductivity measurements and flow measurements. Conductivity measurements are inherently less accurate in order to determine the recovery of solutes which are substantially retained by the membrane. In this regard, conductive salts, typically used as indicators during conductive measurements, can pass through the membrane. Since salts generally pass through the membrane as a percentage of the total salt concentration, changes in local concentration due to concentration gradients or the like can change the conductivity of the product water without necessarily indicating membrane damage. This is especially true in the last stage of a multi-stage cross flow membrane system where salt concentrations (and, therefore, passage of salts as a percentage of that concentration) reach their highest levels. In this regard, the salt passage/percent rejection parameter is generally determined as an average value based on values measured during all stages of the membrane system.

Detailed Description Text (5):

It should be appreciated that the present invention can be utilized with respect to a number of different types of membrane separation processes including, for example, cross flow processes, dead-end flow processes, reverse osmosis, ultrafiltration, microfiltration, nanofiltration, electrodialysis, electrodeionization, pervaporation, membrane extraction, membrane distillation, membrane stripping, membrane aeration and the like or combinations thereof. Reverse osmosis, ultrafiltration, microfiltration and nanofiltration are the preferred membrane separation processes.

Detailed Description Text (15):

Cross-flow filtration techniques, on the other hand, can be used for removing smaller particles (generally about one micron in size or less), colloids and dissolved solutes. Such types of cross-flow membrane separation systems can include, for example, reverse osmosis, microfiltration, ultrafiltration, nanofiltration, electrodialysis or the like. Reverse osmosis can remove even low molecular weight dissolved species that are at least about 0.0001 to about 0.001 microns in minimum diameter, including, for example, ionic and nonionic species, low molecular weight molecules, water-soluble macromolecules or polymers, suspended solids, colloids, and such substances as bacteria and viruses.

Detailed Description Text (21):

3. Membrane separation systems operate at significantly lower temperatures than industrial processes where inverse solubility of solutes is a problem. However, in the case of membrane separation systems such as reverse osmosis and nanofiltration, this low temperature leads to scaling from salts that are less likely to be problematic in higher temperature processes (such as silica and silicate salts). In this regard, typical day-to-day membrane separation operations (for example RO and NF) occur at about 75.degree. F.

Detailed Description Text (131):

Examples of industrial water uses as applied to the present invention include, for example, boiler water production, process water purification and recycle/reuse, softening of raw water, treatment of cooling water blow-down, reclamation of water from papermaking processes, desalination of sea and brackish water for industrial and municipal use, drinking/raw/surface water purification including, for example, the use of membranes to exclude harmful micro-organisms from drinking water, polishing of softened water, membrane bio-reactors, mining and mineral process waters.

Current US Cross Reference Classification (2):

210/652

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L26: Entry 3 of 5

File: USPT

Feb 20, 2001

DOCUMENT-IDENTIFIER: US 6190556 B1

TITLE: Desalination method and apparatus utilizing nanofiltration and reverse osmosis membranes

Detailed Description Text (11):

NF membranes are employed which are designed to selectively reject divalent ions, and the NF elements or cartridges which are used should reject a minimum of about 80%, preferably a minimum of about 90%, more preferably a minimum of about 95%, and most preferably a minimum of about 96% of the divalent ions in an aqueous feed containing about 2,000 ppm of magnesium sulfate and about 2,000 ppm of NaCl, when operated at a pressure of about 70 to 100 psig while producing a flux in the range of about 25-40 GFD. The NF membrane preferably also at least moderately (e.g. about 50 to 55%) reduces the monovalent ion content, and more preferably rejects at least about 60% of the NaCl of such a feed. There are some commercially available membranes meeting these characteristics which produce a divalent ion-depleted permeate and reject monovalent ions in amounts of 70% to 90% at fluxes between about 25 to 40 GFD; these can be purchased either in sheet form or in finished spirally wound cartridges. Examples of such suitable NF membranes are those sold as NF-55, NF-70 and as NF-90 by Dow-Film Tec, as DS-5 and DS-51 by Desalination Systems, Inc., as ESNA-400 by Hydranautics and as TFCS by Fluid Systems, Inc.

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<b>Database:</b>	<div style="border: 1px solid black; padding: 2px;">         US Pre-Grant Publication Full-Text Database          US Patents Full-Text Database          US OCR Full-Text Database          EPO Abstracts Database          JPO Abstracts Database          Derwent World Patents Index          IBM Technical Disclosure Bulletins       </div>
<b>Term:</b>	<div style="border: 1px solid black; padding: 2px;">         6270671.pn.       </div>
<b>Display:</b>	<div style="border: 1px solid black; padding: 2px;">10</div> Documents in <b>Display Format:</b> <div style="border: 1px solid black; padding: 2px;">CIT</div> Starting with Number <div style="border: 1px solid black; padding: 2px;">1</div>
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### Search History

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<i>DB=USPT; PLUR=YES; OP=ADJ</i>			
<u>L29</u>	6270671.pn.	1	<u>L29</u>
<u>L28</u>	5047154.pn.	1	<u>L28</u>
<u>L27</u>	4670150.pn.	1	<u>L27</u>
<u>L26</u>	"nf-90"	5	<u>L26</u>
<u>L25</u>	refining same potable water and nanofiltration	0	<u>L25</u>
<u>L24</u>	L23 and potable water	3	<u>L24</u>
<u>L23</u>	L22 and nanofiltration	39	<u>L23</u>
<u>L22</u>	210/653.ccls.	202	<u>L22</u>
<u>L21</u>	l18 and nanofiltration and drinking water and softening	8	<u>L21</u>
<u>L20</u>	L19 and nf-90	0	<u>L20</u>
<u>L19</u>	L18 and water softening same nanofiltration	11	<u>L19</u>
<u>L18</u>	210/652.ccls.	478	<u>L18</u>
<u>L17</u>	water softening and polyamide same membrane and "nf-90"	0	<u>L17</u>
<u>L16</u>	L13 and nf same membrane	7	<u>L16</u>
<u>L15</u>	L14 and polyamide	1	<u>L15</u>

<u>L14</u>	L13 and potable water	3	<u>L14</u>
<u>L13</u>	L8 and nf same membrane	7	<u>L13</u>
<u>L12</u>	l8 and nanofiltratio	0	<u>L12</u>
<u>L11</u>	l8 and nf-90 and membrane	0	<u>L11</u>
<u>L10</u>	L9 and nanofiltration	1	<u>L10</u>
<u>L9</u>	L8 and drinking water and polyamide same membrane same composite	4	<u>L9</u>
<u>L8</u>	210/257.2.ccls.	441	<u>L8</u>
<u>L7</u>	L1 and film tec	2	<u>L7</u>
<u>L6</u>	L2 and film tec	0	<u>L6</u>
<u>L5</u>	l2 and "Film Tec"	0	<u>L5</u>
<u>L4</u>	L1 and "nf-90"	0	<u>L4</u>
<u>L3</u>	L2 and tfc	3	<u>L3</u>
<u>L2</u>	L1 and polyamide and support same polysulfone	49	<u>L2</u>
<u>L1</u>	membrane and composite and aromatic same piperazine	118	<u>L1</u>

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**Search Results - Record(s) 1 through 10 of 49 returned.**☐ 1. Document ID: US 6878278 B2

L2: Entry 1 of 49

File: USPT

Apr 12, 2005

US-PAT-NO: 6878278

DOCUMENT-IDENTIFIER: US 6878278 B2

TITLE: Composite membrane and method for making the same

DATE-ISSUED: April 12, 2005

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Mickols; William E.	Chanhassen	MN		

US-CL-CURRENT: 210/500.38; 210/490, 210/500.27

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KMOC	Draw D
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☐ 2. Document ID: US 6833073 B2

L2: Entry 2 of 49

File: USPT

Dec 21, 2004

US-PAT-NO: 6833073

DOCUMENT-IDENTIFIER: US 6833073 B2

TITLE: Composite nanofiltration and reverse osmosis membranes and method for producing the same

DATE-ISSUED: December 21, 2004

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Agarwal; Ashok K.	Westlake Village	CA		

US-CL-CURRENT: 210/500.38; 210/490, 210/500.21, 210/652, 264/41, 427/244, 427/245

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KMOC	Draw D
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☐ 3. Document ID: US 6805796 B2

L2: Entry 3 of 49

File: USPT

Oct 19, 2004

US-PAT-NO: 6805796

DOCUMENT-IDENTIFIER: US 6805796 B2

TITLE: Water treatment apparatus

DATE-ISSUED: October 19, 2004

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Hirose; Masahiko	Ibaraki			JP
Hiro; Atsushi	Ibaraki			JP
Wilf; Mark	San Diego	CA		

US-CL-CURRENT: 210/321.76; 210/321.75, 210/500.37, 210/500.38, 210/639, 210/651,  
210/652

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KBAC	Draw De
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☐ 4. Document ID: US 6723241 B2

L2: Entry 4 of 49

File: USPT

Apr 20, 2004

US-PAT-NO: 6723241

DOCUMENT-IDENTIFIER: US 6723241 B2

TITLE: Composite membrane and method for making the same

DATE-ISSUED: April 20, 2004

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Mickols; William E.	Chanhassen	MN		

US-CL-CURRENT: 210/500.38; 210/490, 210/500.27

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KBAC	Draw De
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☐ 5. Document ID: US 6709590 B1

L2: Entry 5 of 49

File: USPT

Mar 23, 2004

US-PAT-NO: 6709590

DOCUMENT-IDENTIFIER: US 6709590 B1

TITLE: Composite reverse osmosis membrane and method for producing the same

DATE-ISSUED: March 23, 2004



## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Hirose; Masahiko	Ibaraki			JP

US-CL-CURRENT: 210/500.38; 210/490, 210/500.37, 427/244, 427/245

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWAC	Draw D
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☐ 6. Document ID: US 6562266 B2

L2: Entry 6 of 49

File: USPT

May 13, 2003

US-PAT-NO: 6562266

DOCUMENT-IDENTIFIER: US 6562266 B2

TITLE: Composite membrane and method for making the same

DATE-ISSUED: May 13, 2003

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Mickols; William E.	Chanhassen	MN		

US-CL-CURRENT: 264/41; 210/500.38, 264/48, 427/244, 427/245

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWAC	Draw D
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☐ 7. Document ID: US 6406626 B1

L2: Entry 7 of 49

File: USPT

Jun 18, 2002

US-PAT-NO: 6406626

DOCUMENT-IDENTIFIER: US 6406626 B1

TITLE: Composite semipermeable membrane, processfor producing the same, and method of purifying water with the same

DATE-ISSUED: June 18, 2002

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Murakami; Mutsuo	Shiga			JP
Tateishi; Yasushi	Kyoto			JP
Fusaoka; Yoshinari	Shiga			JP

US-CL-CURRENT: 210/500.38; 210/500.37, 264/41, 427/244, 427/245

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWAC	Draw D
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☐ 8. Document ID: US 6337018 B1

L2: Entry 8 of 49

File: USPT

Jan 8, 2002

US-PAT-NO: 6337018

DOCUMENT-IDENTIFIER: US 6337018 B1

TITLE: Composite membrane and method for making the same

DATE-ISSUED: January 8, 2002

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Mickols; William E.	Chanhassen	MN		

US-CL-CURRENT: 210/500.38; 210/490, 210/500.27, 264/48, 264/49, 427/244

Full	Title	Citation	Front	Review	Classification	Date	Reference				Claims	KNOW	Drawn De
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☐ 9. Document ID: US 6280853 B1

L2: Entry 9 of 49

File: USPT

Aug 28, 2001

US-PAT-NO: 6280853

DOCUMENT-IDENTIFIER: US 6280853 B1

TITLE: Composite membrane with polyalkylene oxide modified polyamide surface

DATE-ISSUED: August 28, 2001

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Mickols; William E.	Chanhassen	MN		

US-CL-CURRENT: 428/474.4; 210/490, 210/500.23, 210/500.33, 210/500.35, 210/651,  
210/652, 210/653, 210/654, 428/474.9, 428/475.5, 428/475.8, 428/476.1

Full	Title	Citation	Front	Review	Classification	Date	Reference				Claims	KNOW	Drawn De
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☐ 10. Document ID: US 6245234 B1

L2: Entry 10 of 49

File: USPT

Jun 12, 2001

US-PAT-NO: 6245234

DOCUMENT-IDENTIFIER: US 6245234 B1

TITLE: Composite polyamide reverse osmosis membrane and method of producing the same

DATE-ISSUED: June 12, 2001

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Koo; Ja-Young	Acton	MA		
Kim; Jong-Eun	Jeju-si			KR
Kim; Wan-Ju	Taejun			KR
Park; Ki Suop	Suwon			KR

US-CL-CURRENT: 210/500.38; 210/490, 210/500.27, 264/41, 427/244, 427/245

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KUMC	Draw D
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L2: Entry 11 of 49

File: USPT

Jan 9, 2001

US-PAT-NO: 6171497

DOCUMENT-IDENTIFIER: US 6171497 B1

TITLE: Highly permeable composite reverse osmosis membrane

DATE-ISSUED: January 9, 2001

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Hirose; Masahiko	Shiga			JP
Ohara; Tomomi	Shiga			JP
Ando; Masaaki	Shiga			JP

US-CL-CURRENT: 210/500.38; 210/321.6, 210/321.74, 210/321.75, 210/490

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWIC	Draw D.
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☐ 12. Document ID: US 6024873 A

L2: Entry 12 of 49

File: USPT

Feb 15, 2000

US-PAT-NO: 6024873

DOCUMENT-IDENTIFIER: US 6024873 A

TITLE: Highly permeable composite reverse osmosis membrane and a reverse osmosis membrane module using the same

DATE-ISSUED: February 15, 2000

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Hirose; Masahiko	Shiga			JP
Ito; Hiroki	Shiga			JP
Ohara; Tomomi	Shiga			JP

US-CL-CURRENT: 210/500.38; 210/321.6, 210/490, 210/500.37, 210/500.42

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWC	Draw D
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☐ 13. Document ID: US 5922203 A

L2: Entry 13 of 49

File: USPT

Jul 13, 1999

US-PAT-NO: 5922203

DOCUMENT-IDENTIFIER: US 5922203 A

TITLE: Amine monomers and their use in preparing interfacially synthesized  
membranes for reverse osmosis and nanofiltration

DATE-ISSUED: July 13, 1999

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Tomaschke; John E.	San Diego	CA		

US-CL-CURRENT: 210/500.37; 210/490, 210/500.38, 210/500.39, 264/41, 427/244,  
427/245

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWC	Draw D
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☐ 14. Document ID: US 5843351 A

L2: Entry 14 of 49

File: USPT

Dec 1, 1998

US-PAT-NO: 5843351

DOCUMENT-IDENTIFIER: US 5843351 A

TITLE: Highly permeable composite reverse osmosis membrane, method of producing the  
same

DATE-ISSUED: December 1, 1998

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Hirose; Masahiko	Shiga			JP
Ito; Hiroki	Shiga			JP
Maeda; Masatoshi	Osaka			JP
Tanaka; Kazuo	Shiga			JP

US-CL-CURRENT: 264/45.1; 210/490, 210/500.38, 264/41, 264/48

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWC	Draw D
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☐ 15. Document ID: US 5783079 A

L2: Entry 15 of 49

File: USPT

Jul 21, 1998

US-PAT-NO: 5783079

DOCUMENT-IDENTIFIER: US 5783079 A

TITLE: Composite hollow fiber membrane and process for its production

DATE-ISSUED: July 21, 1998

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Kumano; Atsuo	Otsu			JP
Oguro; Hiroshi	Otsu			JP
Hayashi; Takafumi	Otsu			JP

US-CL-CURRENT: 210/500.23; 210/490, 210/500.38, 210/500.39, 210/500.41, 264/127,  
427/244, 427/245, 427/246

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWIC	Draw Da
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☐ 16. Document ID: US 5755964 A

L2: Entry 16 of 49

File: USPT

May 26, 1998

US-PAT-NO: 5755964

DOCUMENT-IDENTIFIER: US 5755964 A

TITLE: Method of treating polyamide membranes to increase flux

DATE-ISSUED: May 26, 1998

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Mickols; William E.	Midland	MI		

US-CL-CURRENT: 210/500.37; 210/490, 210/500.38, 264/48

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWIC	Draw Da
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☐ 17. Document ID: US 5744039 A

L2: Entry 17 of 49

File: USPT

Apr 28, 1998

US-PAT-NO: 5744039

DOCUMENT-IDENTIFIER: US 5744039 A

TITLE: Composite semipermeable membrane and production method thereof

DATE-ISSUED: April 28, 1998

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
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Itoh; Hiroki	Osaka	JP
Hirose; Masahiko	Osaka	JP
Ishii; Katsumi	Osaka	JP

US-CL-CURRENT: 210/644; 210/500.38, 210/506, 427/244

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWIC	Draw D
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☐ 18. Document ID: US 5733602 A

L2: Entry 18 of 49

File: USPT

Mar 31, 1998

US-PAT-NO: 5733602

DOCUMENT-IDENTIFIER: US 5733602 A

TITLE: Method for producing highly permeable composite reverse osmosis membrane

DATE-ISSUED: March 31, 1998

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Hirose; Masahiko	Osaka			JP
Ito; Hiroki	Osaka			JP
Ohara; Tomomi	Osaka			JP

US-CL-CURRENT: 427/245; 427/255.6, 427/301, 427/340

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWIC	Draw D
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☐ 19. Document ID: US 5693227 A

L2: Entry 19 of 49

File: USPT

Dec 2, 1997

US-PAT-NO: 5693227

DOCUMENT-IDENTIFIER: US 5693227 A

TITLE: Catalyst mediated method of interfacial polymerization on a microporous support, and polymers, fibers, films and membranes made by such method

DATE-ISSUED: December 2, 1997

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Costa; Lawrence C.	Mansfield	MA		

US-CL-CURRENT: 210/650; 210/490, 210/500.38, 427/245, 95/45, 96/14

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWIC	Draw D
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☐ 20. Document ID: US 5658460 A

L2: Entry 20 of 49

File: USPT

Aug 19, 1997

US-PAT-NO: 5658460

DOCUMENT-IDENTIFIER: US 5658460 A

TITLE: Use of inorganic ammonium cation salts to maintain the flux and salt rejection characteristics of reverse osmosis and nanofiltration membranes during drying

DATE-ISSUED: August 19, 1997

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Cadotte; John E.	Minnetonka	MN		
Batzel; Daniel A.	Glenview	IL		
Stocker; Thomas F.	San Diego	CA		

US-CL-CURRENT: 210/500.38; 210/490, 210/500.37, 264/45.1, 264/48

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	K00C	Draw D
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File: USPT

Apr 12, 2005

DOCUMENT-IDENTIFIER: US 6878278 B2

TITLE: Composite membrane and method for making the sameAbstract Text (1):

A composite membrane and method for making the same, comprising a porous support and a polyamide surface. The subject membrane provides improved flux and/or rejection rates. The subject membrane is further capable of operating at lower operating pressures. The subject method includes reacting a polyfunctional amine with a polyfunctional acyl halide to form a polyamide. The method includes the step of contacting a complexing agent with the polyfunctional acyl halide prior substantial reaction between the polyfunctional acyl halide and a polyfunctional amine. The subject process is easily adapted to commercial scale manufacturing processes and is particularly suited for making nanofiltration and reverse osmosis composite membranes.

Brief Summary Text (2):

Reverse osmosis and nanofiltration membranes are used to separate dissolved or dispersed materials from feed streams. The separation process typically involves bringing an aqueous feed solution into contact with one surface of the membrane under pressure so as to effect permeation of the aqueous phase through the membrane while permeation of the dissolved or dispersed materials is prevented.

Brief Summary Text (3):

Both reverse osmosis and nanofiltration membranes typically include a thin film discriminating layer fixed to a porous support, collectively referred to as a "composite membrane". Ultrafiltration and microfiltration membranes may also have a composite arrangement. The support provides physical strength but offers little resistance to flow due to its porosity. On the other hand, the discriminating layer is less porous and provides the primary means of separation of dissolved or dispersed materials. Therefore, it is generally the discriminating layer which determines a given membrane's "rejection rate"--the percentage of the particular dissolved material (i.e., solute) rejected, and "flux"--the flow rate per unit area at which the solvent passes through the membrane.

Brief Summary Text (4):

Reverse osmosis membranes and nanofiltration membranes vary from each other with respect to their degree of permeability to different ions and organic compounds. Reverse osmosis membranes are relatively impermeable to virtually all ions, including sodium and chlorine ions. Therefore, reverse osmosis membranes are widely used for the desalination of brackish water or seawater to provide relatively non-salty water for industrial, commercial, or domestic use because the rejection rate of sodium and chlorine ions for reverse osmosis membranes is usually from about 95 to about 100 percent.

Brief Summary Text (5):

Nanofiltration membranes are usually more specific for the rejection of ions. Generally, nanofiltration membranes reject divalent ions, including radium, magnesium, calcium, sulfate, and carbonate. In addition, nanofiltration membranes are generally impermeable to organic compounds having molecular weights above about 200 Daltons. Additionally, nanofiltration membranes generally have higher fluxes at

comparable pressures than reverse osmosis membranes. These characteristics render nanofiltration membranes useful in such diverse applications as the "softening" of water and the removal of pesticides from water. As an example, nanofiltration membranes generally have a sodium chloride rejection rate of from about 0 to about 95 percent but have a relatively high rejection rate for salts such as magnesium sulfate and in some cases organic compounds such as atrazine.

Brief Summary Text (6):

Among particularly useful membranes for reverse osmosis and nanofiltration applications are those in which the discriminating layer is a polyamide. The polyamide discriminating layer for reverse osmosis membranes is often obtained by an interfacial polycondensation reaction between a polyfunctional amine monomer and a polyfunctional acyl halide monomer (also referred to as, polyfunctional acid halide) as described in, for example, U.S. Pat. No. 4,277,344, which is incorporated herein by reference. The polyamide discriminating layer for nanofiltration membranes is typically obtained via an interfacial polymerization between a piperazine or an amine substituted piperidine or cyclohexane and a polyfunctional acyl halide as described in U.S. Pat. Nos. 4,769,148 and 4,859,384, both incorporated in their entirety by reference. Another way of obtaining polyamide discriminating layers suitable for nanofiltration is via the methods described in, for example, U.S. Pat. Nos. 4,765,897; 4,812,270; and 4,824,574. These patents describe changing a reverse osmosis membrane, such as those of U.S. Pat. No. 4,277,344, into a nanofiltration membrane.

Brief Summary Text (7):

Composite, polyamide membranes are typically prepared by coating a porous support with a polyfunctional amine monomer, most commonly coated from an aqueous solution. Although water is a preferred solvent, non-aqueous solvents may be utilized, such as acetyl nitrile and dimethylformamide (DMF). A polyfunctional acyl halide monomer (also referred to as acid halide) is subsequently coated on the support, typically from an organic solution. Although no specific order of addition is necessarily required, the amine solution is typically coated first on the porous support followed by the acyl halide solution. Although one or both of the polyfunctional amine and acyl halide may be applied to the porous support from a solution, they may alternatively be applied by other means such as by vapor deposition, or neat.

Brief Summary Text (8):

Means for improving the performance of membranes by the addition of constituents to the amine and/or acyl halide solutions are described in the literature. For example, U.S. Pat. No. 4,950,404, issued to Chau, describes a method for increasing flux of a composite membrane by adding a polar aprotic solvent and an optional acid acceptor to the aqueous amine solution prior to interfacially polymerizing the amine with an polycarboxylic acid halide. Similarly, U.S. Pat. Nos. 6,024,873; 5,989,426; 5,843,351; 5,733,602; 5,614,099; and 5,576,057 to Hirose, et al. describes the addition of selected alcohols, ethers, ketones, esters, halogenated hydrocarbons, nitrogen-containing compounds and sulfur-containing compounds having a solubility parameter of 8 to 14 (cal/cm<sup>3</sup>)<sup>1/2</sup> to the aqueous amine solution and/or organic acid halide solution prior to interfacial polymerization.

Brief Summary Text (9):

Methods of improving membrane performance by post-treatment are also known. For example, U.S. Pat. No. 5,876,602 to Jons, et al. describes treating a polyamide composite membrane with an aqueous chlorinating agent to improve flux, lower salt passage, and/or increase membrane stability to base. U.S. Pat. No. 5,755,964 to Mickols discloses a process wherein the polyamide discriminating layer is treated with ammonia or selected amines, e.g., butylamine, cyclohexylamine, and 1,6 hexane diamine. U.S. Pat. No. 4,765,897 to Cadotte discloses the post treatment of a membrane with a strong mineral acid followed by treatment with a rejection enhancing agent. U.S. Pat. Nos. 4,765,897; 5,876,602 and 5,755,964 are incorporated herein by reference.

Brief Summary Text (10):

Membranes having higher flux at standard operating pressures, or which are capable of maintaining flux at relatively lower operating pressures are desired. Moreover, membranes having higher rejection rates while achieving improved flux and/or lower pressure requirements are also desired. Methods for making such membranes, particularly those readily adaptable to commercial scale membrane fabrication are also desired.

Brief Summary Text (12):

The present invention provides an improved composite membrane and method for making the same by interfacially polymerizing a polyfunctional amine and a polyfunctional acyl halide on at least one surface of a porous support to form a polyamide layer thereon. The method is characterized by the step of contacting a complexing agent with the polyfunctional acyl halide prior to and/or during the reaction between the polyfunctional acyl halide and polyfunctional amine.

Brief Summary Text (13):

An object of the present invention is to provide improved membranes having higher flux and/or more preferred rejection characteristics (i.e., higher or lower depending upon the intended end use of the membrane). A further object of the present invention is to provide membranes capable of operating at relatively lower pressures while still providing a given flux and/or rejection. Still another object of the present invention is to provide methods for making such membranes, including methods which are readily adaptable to commercial scale membrane manufacturing. The subject method is particularly suited for making nanofiltration and reverse osmosis membranes.

Detailed Description Text (2):

Composite membranes of the present invention are prepared by interfacially polymerizing a polyfunctional amine monomer (also referred to herein as "amine", "polyamine", and "polyfunctional amine"--wherein each term is intended to refer both to the use of a single species or multiple species of amines in combination) with a polyfunctional acyl halide (also referred to as "acyl halide", "acid halide", polyfunctional acid halide--wherein each term is intended to refer both to the use of a single species or multiple species of acyl halides in combination) on at least one surface of a porous support. The amine and acyl halide are typically delivered to the porous support by way of a coating step from solution wherein the amine is typically coated from an aqueous solution and the acyl halide is coated from a non-aqueous, organic-based solution. Although the coating steps can be "non-sequential", i.e., follow no specific order, the amine is preferably coated on the support first followed by the acyl halide. Coating may be accomplished by spraying, rolling, use of a dip tank, etc. Excess solution may be removed from the support by air and/or water knife, dryers, ovens, etc.

Detailed Description Text (3):

The polyfunctional amine monomer used in the present invention may have primary or secondary amino groups and may be aromatic (e.g., m-phenylenediamine, p-phenylenediamine, 1,3,5-triaminobenzene, 1,3,4-triaminobenzene, 3,5-diaminobenzoic acid, 2,4-diaminotoluene, 2,4-diaminoanisole, and xylylenediamine) or aliphatic (e.g., ethylenediamine, propylenediamine, and tris(2-diaminoethyl)amine). Examples of preferred amine species include primary aromatic amines having two or three amino groups, most especially m-phenylene diamine, and secondary aliphatic amines having two amino groups, most especially piperazine. The amine is typically applied to the microporous support as a solution in water. The aqueous solution most commonly contains from about 0.1 to about 20 weight percent and more preferably from about 0.5 to about 6 weight percent amine. Once coated on the microporous support, excess aqueous amine solution may be optionally removed. The amine solution need not be aqueous but is preferably immiscible with the non-polar non-aqueous solvent described below.

Detailed Description Text (5):

Once brought into contact with one another, the polyfunctional acyl halide and polyfunctional amine react at their surface interface to form a polyamide discriminating layer. The reaction time is typically less than one second but contact time is often from one to sixty seconds, after which excess liquid may optionally be removed, e.g., by way of an air knife, water bath(s), dryer and the like. The removal of the excess water and/or organic solvent is most conveniently achieved by drying at elevated temperatures, e.g., from about 40.degree. C. to about 120.degree. C., although air drying at ambient temperatures may be used.

Detailed Description Text (6):

While not wishing to be bound by theory, it is believed that the acyl halide functional groups of the polyfunctional acyl halide monomer often become hydrolyzed prior to contact with amine functional groups. Under typical manufacturing conditions, such hydrolysis of acyl halide functional groups is substantially irreversible. That is, under the time, temperature and concentrations typically used in commercial scale membrane manufacturing, amine functional groups are not believed to substantially react with hydrolyzed acyl halide groups. It is believed that such hydrolysis of acyl halide groups leads to compromised membrane performance.

Detailed Description Text (7):

While not wishing to be bound by theory, it is believed that the subject complexing agents are capable of forming "associations" with the polyfunctional acyl halide monomers when utilized in accordance with the subject method. It is believed that the formation of such associations significantly reduce hydrolysis of the acyl halide functional groups and permits sufficient subsequent reaction between the acyl halide and amine functional groups thereby resulting in the aforementioned improvements, in membrane performance.

Detailed Description Text (16):

Associations which are too weak (i.e., have a total energy value less about 3.5 kcals/mole) result in associations that do not effectively prevent hydrolysis of the acyl halide functional groups. As will be described below, one measure of a sufficiently strong association is the presence of a "detectable quantity" of "retained" complexing agent within the polyamide, even after post washing of the membrane. On the other hand, associations which are too strong (i.e., have a total energy of more than about 20 or preferably 15 kcals/mole) do not permit sufficient displacement and reaction by amines during membrane formation, thus preventing the formation of the desired polyamide. An example of an association which is too strong is the hydrolysis of an acid chloride group of TMC under common manufacturing conditions which results in a total energy value of greater than about 25 kcals/mole.

Detailed Description Text (22):

One means for determining whether the subject complexing agent(s) have been successfully contacted with the acyl halide in accordance to the subject method is the presence of a "detectable quantity" of "retained" complexing agent in the polyamide membrane. The term "retained" is intended to mean complexing agent which remains (e.g., associated, covalently bonded, complexed, weakly bound, etc.) within the polyamide membrane even after the membrane has been subjected to operation in reverse osmosis mode using pure water feed at a 24 gfd (gallons per square foot per day) (0.0011 cm/sec) flux rate through the membrane with a permeate recovery between 0.5% to 25% at 25.degree. C. for 24 hours. This may be accomplished by use of test cells commonly used to test membranes. For example, the test cell may be of a "plate and frame" design or may include preparing a spiral wound element with the membrane.

Detailed Description Text (23):

Cleaning with pure water, e.g., passing pure water across the polyamide membrane at 25.degree. C. for 24 hours at a pressure of about 70 pounds per square inch. Such cleaning removes transient sources of materials which may be initially present but which do not contribute to the subject invention. For example, it is well known that phosphoric acid may be added to the amine solution as a pH buffer. In such embodiments some portion of the phosphoric acid may be present on the initial resulting membrane; however, as the phosphoric acid is not contacted with the acyl halide in manner which permits sufficient association, the phosphoric acid is not retained and is washed away from the membrane upon use or cleaning. Although such prior art uses of phosphoric acid may be used in conjunction with the subject invention, such prior art embodiments do not result in "retained" phosphorous, nor the degree of improved membrane performance attributed to the subject invention.

Detailed Description Text (24):

The term "detectable quantity" is intended to mean a sufficient quantity of retained complexing agent is present such that it may be measured, identified or otherwise detected by quantitative or qualitative analysis. Detection of such complexing agents in membranes can be made by way of any suitable analytical technique; however due to the relatively low quantities of complexing agent typically utilized, relatively sensitive analytical techniques are preferred, e.g., gas chromatography, X-ray fluorescence, (XRF), secondary ion mass spectroscopy, IR, and colorimetric analysis of the fully combusted polyamide. Detection of the complexing agent typically focuses upon the binding core of the complexing agent. As described in more detail below, the binding core often comprises metals, e.g. Pb, Fe, Cr, Ni, Co, Cu, Zn, Al, As, Sb, Te, etc. but may include other elements, e.g. P, Si, Se, Ge, etc. One specific X-ray fluorescence detection methodology is particularly well suited for detecting phosphorous containing complexing agents and involves extracting a portion (e.g., 100 mg) of the polyamide polymer from the porous support, e.g., boiling the membrane in water for about 30 minutes followed by dissolving the porous support with an appropriate solvent, e.g., methylene chloride, and subsequently extensively extracting the polyamide in the same solvent. The polyamide may then be isolated and pressed into a 13 mm diameter disk using a die and an hydraulic press (10,000 lbs. load). The resulting disk may be placed between two layers of polypropylene sample support film (6.0 micron thickness) and attached to a Chemplex 30 mm diameter XRF sample cup using a standard support ring. The sample can be measured in a plastic insert with a Pb mask. Measurements can be obtained on both sides of the disk and averaged together. Once prepared, the sample can be analyzed with a Philips PW1480 wavelength dispersive X-ray fluorescence spectrometer equipped with a scandium anode 3 KW X-ray tube. For example, phosphorous can be measured by utilizing K alpha X-ray intensity with the instrument operated under the following conditions: 50 kV, 50 mA, germanium crystal (2d=6.532 angstroms), gas flow proportional detector (argon/methane), upper and lower discriminator level 80/25, He purge. The phosphorous K alpha peak can be measured at a 2 theta angle of 141.035 and backgrounds can be measured at + and - offsets of 1.5. Peak and background measurements are commonly taken for 10 seconds each.

Detailed Description Text (25):

In preferred embodiments, the subject polyamide composite membrane includes at least about 25 micrograms (and preferably at least 50 micrograms, more preferably 100 micrograms and in some embodiments at least 200 micrograms) of the binding core of the complexing agent "retained" for every gram of polyamide. The elements that constitute the binding core of the subject complexing agents are not typically present during conventional membrane preparation. As such, these elements serve as a good indicator as to whether the subject complexing agents have been used effectively during membrane preparation.

Detailed Description Text (26):

As indicated, the retained complexing agent is believed to be a result of the formation of a complex between the complexing agent and the polyamide, retained

monomers, and/or reaction products. Although dependent upon the relative density of the polyamide layer, most membranes of the subject invention will include at least 0.02 micrograms of complexing agent per square meter of membrane, but more commonly more than about 1 microgram of complexing agent per square meter of membrane.

Detailed Description Text (27):

The complexing agents of the present invention are not particularly limited and different species of compounds may be used in combination. However, preferred species are non-pyrophoric, sufficiently stable in air and water (i.e., the species do not decompose, degrade or significantly react with water or air within the time period of the subject method), and have suitable industrial hygiene properties, e.g., do not pose significant environmental hazards, do not require expansive handling requirements, do not pose significant safety concerns, etc. The subject complexing agents are preferably "substantially soluble" in the organic solutions as described herein. The term "substantially soluble" is intended to mean that a sufficient quantity of the complexing agent dissolves in the solution to result in a final membrane having improved flux, rejection and/or lower operating pressure as compared to an identical membrane prepared without the subject complexing agent. An additional indicia that the complexing agent is "substantially soluble" is the presence of a detectable quantity of retained complexing agent in the polyamide layer. When used at effective concentrations the subject complexing agents preferably dissolve and form a single homogeneous phase within the organic solutions previously described. Preferred complexing agents have a solubility parameter of from about 15 to about 26, and more preferably from 18 to 23 J.sup.1/2 cm.sup.-3/2.

Detailed Description Text (29):

Unlike conventional interfacial polymerization of polyfunctional acyl halide and polyfunctional amines in which the relative concentration of the acyl halide species is rate controlling, in the present invention the relative concentration of the amine species may take on a more significant role. Through routine experimentation, those skilled in the art will appreciate the optimum concentration of polyfunctional amine, given the specific nature and concentration of the complexing agent(s), acyl halide, and amine, reaction conditions and desired membrane performance.

Detailed Description Text (59):

The material of construction of the porous support of the composite membrane is not critical to the invention. Any porous support that provides physical strength to the discriminating layer may be employed, so long as the pore sizes are sufficiently large to permit the unhindered passage of permeate but not so large as to interfere with the bridging-over of the resulting discriminating layer. Typical pore sizes will range from 10 to 1,000 nanometers. Typical support materials that are known in the art include cellulose esters, polysulfones, polyether sulfones, polyvinyl chloride, chlorinated polyvinyl chloride, polyvinylidene fluoride, polystyrenes, polycarbonates, polyimides, polyacrylonitriles, and polyesters. A particularly preferred class of support materials are polysulfones. Preparation of such supports are described in U.S. Pat. Nos. 3,926,798; 4,039,440; and 4,277,344, all of which are incorporated herein by reference. The thickness of the microporous support is usually 25 to 125 micrometers, and preferably from 40 to 75 micrometers.

Detailed Description Text (60):

A variety of membrane shapes are commercially available and useful in the present invention. These include spiral wound, hollow fiber, tubular, or flat sheet type membranes. In regard to the composition of the membrane, often the discriminating layer has hygroscopic polymers other than the polyamide coated upon the surface of the discriminating layer. Among these polymers are anionic, cationic, neutral and zwitterionic such as polymeric surfactants, polyvinyl alcohol, polyethylene imine and polyacrylic acid.

Detailed Description Text (61):

The membranes of the present invention may be subjected to various post treatments as described in U.S. Pat. Nos. 4,765,897; 5,876,602 and 5,755,964, all of which are incorporated herein by reference. Such post treatments may further enhance membrane performance, e.g., increased flux and/or decreased salt passage.

Detailed Description Text (62):

For example, as described in U.S. Pat. No. 5,876,602, membrane stability to strong base exposure (while maintaining flux and salt passage) can be achieved by contacting the membrane, after it has been formed on a porous support, whether in flat sheet or element form, with a hypochlorite solution at a pH of at least 10.5. The optimal exposure time depends on the temperature and concentration of the hypochlorite used. At room temperature, conditions which achieve the stated goals can generally be found within the ranges of 10 minutes to 5 hours and at concentrations of 200 to 10,000 ppm by weight of hypochlorite, measured as chlorine. Preferred concentrations of hypochlorite are 500 to 7,000 ppm; preferred exposure times are 30 minutes to three hours. In a preferred embodiment the membrane is subjected to a heat treatment before being exposed to the aforementioned chlorine treatment. The membranes are heated in water at a temperature of 40.degree. C. to 100.degree. C. for times of 30 seconds to 24 hours. The heat treatment results in a further lowering of the salt passage and the removal of impurities contained in the membrane which otherwise may interfere in the beneficial results of the chlorine treatment. Depending on the application desired, the two treatment conditions can be adjusted within the ranges stated such that the salt passage is improved while maintaining or even improving flux over either treatment alone. The order in which the two treatments are conducted is critical since heat treating the membrane simultaneously with or subsequently to the chlorine treatment does not provide the improved results obtained by first heat treating the membrane followed by the chlorine treatment.

Detailed Description Text (63):

Another example of an applicable post treatment is described in U.S. Pat. No. 5,755,964, which comprises contacting the discriminating layer with an amine from the group consisting of: ammonia optionally substituted with one or more alkyl groups of one to two carbons which alkyl groups may be further optionally substituted with one or more substituents selected from hydroxy, phenyl, or amino; butylamine; cyclohexylamine; 1,6-hexanediamine and mixtures thereof. Preferred substituted ammonia substances include those such as dimethylamine; trimethylamine; ethylamine; triethanolamine; N,N-dimethyl ethanolamine; ethylenediamine; and benzylamine. It has been discovered that by contacting the above amines with the discriminating layer, the flux is increased and the rejection rates for particular substances may be changed. The degree that the flux of the membrane is increased or enhanced may be controlled by varying the particular amine employed, the concentration of the amine, the time of contact between the discriminating layer and amine, the temperature of the contact, the pH of the amine solution, or combinations thereof. As the flux is increased, the selectivity of the membrane may change, i.e., the membrane may allow univalent ions such as sodium to pass through the membrane at a higher rate while only rejecting divalent ions and organic compounds.

Detailed Description Text (64):

The amine used to treat the polyamide discriminating layer may be in solution, neat, or even a gas phase so long as it can be contacted with the polyamide. Gas phases may typically be employed for lower molecular weight amines such as ammonia, methylamine, and dimethylamine. The solvent may be any solvent in which the amine is soluble so long as the flux enhancement and the performance of the membrane is not hindered by contact with the solvent. Typical solvents may include water and organic compounds such as alcohols and hydrocarbons provided the support is not dissolved by the solvent. Generally, because of its ease of handling and its



availability, water is employed if a solvent is desired.

Detailed Description Text (65):

The extent that the flux of the membrane is enhanced when treated with the amines of this invention varies depending upon the particular amine employed. At least one general trend applies in most situations, however. The trend being that the more functional groups which are present on the amine, e.g., alcohol and/or amino groups, the greater the increase in flux. Correspondingly, the concentration of the amine and time of contact are interrelated and affect the degree of flux enhancement. The minimum length of time that a particular amine is required to be contacted with the discriminating layer for an increase in flux depends to a great extent upon the concentration of the amine. Generally, the higher the concentration of the amine, the shorter the necessary length of contacting time to increase the flux. In most cases, the concentration of the amine should be at least about 5, preferably at least about 20, most preferably at least about 50, to about 100 percent by weight. The minimum time of contact can be from at least about 15 seconds, preferably at least about one minute, more preferably at least about 30 minutes when contacted at ambient temperatures.

Detailed Description Text (66):

In general, the longer the time of contact and the higher the concentration of the amine, the greater the increase in flux. After a prolonged time of contact, the flux will reach its maximum increase and no longer increase. At this point, the membrane may be used or continued to be stored in the amine. The time to reach the maximum increase varies depending upon the particular amine employed, the concentration of the amine, and the temperature of contact but is ascertainable by one skilled in the art without undue experimentation by utilizing the general trends disclosed above. For most amines and concentrations, the flux of the membrane will be maximized once the discriminating layer has been contacted for about 5 days with the amine. If it is desired to shorten the minimum length of time of contact, then the surface temperature of the polyamide discriminating layer may be increased. Although this applies generally, it is particularly advantageous if low concentrations of an amine which might require a long contacting time are being employed. Although temperature from about 0.degree. to about 30.degree. C. are most conveniently used, increased temperatures may shorten the necessary contacting time. The increased temperatures should not be so high that the membrane's performance is reduced, i.e., not above about 130.degree. C. Typical temperatures which will hasten the flux effect of the membrane are from at least about 30.degree. C., preferably at least about 60.degree. C. to about 130.degree. C. These temperatures may be reached by contacting the amine with the polyamide discriminating layer in a device such as an oven or a dryer. Typical ovens or dryers which may be employed include convection, infrared, or forced air dryers.

Detailed Description Text (67):

The pH of the amine solution to be contacted with the polyamide is not a critical aspect of the invention. However, the pH should not be so low that the particular amine being employed precipitates out of solution. On the other hand, the pH should not be so high that the polyamide discriminating layer is degraded or performance is negated. Preferably, a pH of about 7 to about 12 is useful in the method of the present invention and for some amines higher pHs may increase the degree of flux enhancement.

Detailed Description Text (68):

The method used to contact the amine with the discriminating layer may be any which allows the amine to become associated with the polyamide for a sufficient time to increase the flux. For instance, the polyamide may be partially or totally immersed or soaked in the amine or amine solution. The amine or amine solution may also be passed through, sprayed onto, or rolled onto the discriminating layer. Although the aforementioned methods may also be useful when the amine is a gas, the contacting of a gaseous amine with the discriminating layer is advantageously accomplished in



a closed vessel to minimize the amount of amine employed.

Detailed Description Text (69):

Improved flux and rejection properties can also be achieved by post treating the subject membranes by contacting the membranes with a strong mineral acid, e.g., phosphoric acid, polyphosphoric acid, phosphorous acid, sulfuric acid, etc. Phosphoric acid at concentrations of from about 10 to about 85 weight percent are particularly preferred. As described in U.S. Pat. No. 4,765,987, the membrane may be contacted with the mineral acid, e.g., by spraying an aqueous acid solution onto the membrane, dipping the membrane in an aqueous acid bath, etc. In some embodiments the acid solution may be heated. Once treated with the mineral acid, the membrane may be further treated with the rejection enhancing agents, e.g., colloids, tannic acid, polyamidoamines, etc, as described in U.S. Pat. No. 4,765,897.

Detailed Description Text (70):

As used herein the following terms have the definitions provided: "rejection rate" is the percentage of a particular dissolved or dispersed material (i.e., solute) which does not flow through the membrane with the solvent. The rejection rate is equal to 100 minus the percentage of dissolved or dispersed material which passes through the membrane, i.e., solute passage, "salt passage" if the dissolved material is salt. "Flux" is the flow rate per unit area at which solvent, typically water, passes through the membrane. "Reverse osmosis membrane" is a membrane which has a rejection rate for NaCl of from about 95 to about 100 percent.

"Nanofiltration membrane" is a membrane which has a rejection rate for NaCl of from about 0 to about 95 percent and has a rejection rate for at least one divalent ion or organic compound of from about 20 to about 100 percent. "Polyamide" is a polymer in which amide linkages (--C(O)NH--) occur along the molecular chain. "Complexing agent", "amine" and "acyl halide" are intended to mean a single species or multiple species of compounds intermixed. For example, the term "amine" may make reference to a mixture of polyfunctional amine monomers. The terms "percent by weight", "percent weight" and "weight percent" are intended to mean 100.times.(gram of solute/100 milliliters of solvent).

Detailed Description Text (72):

The following examples are intended to help illustrate the invention and should not be construed to limit the scope of the appended claims. Except where indicated otherwise, composite membranes were made in the laboratory using a porous polysulfone support formed from a 16.5 percent polysulfone solution in DMF. The support was cut into rectangles (11 in. by 7 in.), clipped onto wire frames (10 in. by 7.5 in.) and placed in a 2.5 weight percent meta phenylene diamine (MPD) solution for approximately 20 minutes. The MPD soaked supports were then placed on a paper towel and rolled with a rubber roller to remove excess solution from both the back and front sides. The support was then placed on a plastic sheet and a silicone rubber gasket placed around the edge. A plastic sheet was cut with the opening being the same size as the opening in the gasket. This was clamped to form a leak proof seal at the edge. 50 ml of a Isopar L solution of trimesoyl chloride (TMC) (0.09 weight percent) containing a 1:2 stoichiometric ratio (TMC:complexing agent) of the complexing agent of interest was then poured on top. The specific complexing agent utilized in each example is provided in the Tables below. Control samples contained no complexing agent. After 1 minute of reaction, the TMC solution was poured off and the membrane was rinsed with hexane and allowed to dry for the period of time specified in the Tables below. The formed composite membrane was then placed in water and tested using a 2000 ppm NaCl solution with a pH between 6.5 and 8 at 130 psi applied pressure. The membranes were run under these test conditions for 30 min and then the permeate was collected and analyzed. The results are provided in the Tables below. Due to the variability in preparation and testing conditions, a separate control membrane was prepared and tested with each prepared batch of membranes, as indicated in each Table below.

Detailed Description Text (76):

As shown in the Tables provided above, the addition of the subject complexing agents to the polyfunctional acyl halide solution can improve flux and/or rejection (e.g., salt passage) of the resulting membranes.

Other Reference Publication (2):

Derwent Abstract, JP2000015067A, Manufacture of Composite Semipermeable Membrane Recovery of Electrode Deposition Paints and Pure Water for Washing Semiconductor, etc., with available selected translated excerpts from patent.

## CLAIMS:

1. A composite membrane comprising a polyamide layer fixed upon a porous support wherein the polyamide layer comprises a complexing agent having a solubility parameter of from about 15 to about 26 J.sup.1/2 cm .sup.-3/2 and the complexing agent has a binding core selected from non-sulfur atoms selected from Groups IIIA-VIB and Periods 3-6 of the conventional IUPAC period table, wherein said complexing agent remains detectable within the polyamide layer after the membrane has been operated in reverse osmosis mode using pure water feed at a 24 gfd flux rate through the membrane with a permeate recovery between 0.5% to 25% at 25.degree. C. for 24 hours.
2. The membrane of claim 1 wherein said polyamide layer includes at least 25 micrograms of said binding core per gram of polyamide.
3. The membrane of claim 2 wherein said polyamide layer includes at least 50 micrograms of said binding core per gram of polyamide.
4. The membrane of claim 3 wherein said polyamide layer includes at least 200 micrograms of said binding core per gram polyamide.
5. A composite membrane comprising a polyamide layer fixed upon a porous support wherein the polyamide layer comprises a complexing agent having a solubility parameter of front about 15 to about 26 J.sup.1/2 cm.sup.-3/2 and the complexing agent has a binding core selected from non-sulfur metal, wherein said complexing agent remains detectable within the polyamide layer after the membrane has been operated in reverse osmosis mode using pure water feed at a 24 gfd flux rate through the membrane with a permeate recovery between 0.5% to 25% at 25.degree. C. for 24 hours.
6. The membrane of claim 5 wherein said binding core is selected from at least one of the following elements: Al, Si, As, Sb, Se, Ta, Fe, Cr, Co, Ni, Cu, and Zn.
7. The membrane of claim 5 wherein said binding core is selected from: silicon and selenium.
8. The membrane of claim 5 wherein said binding core is phosphorous.
9. The membrane of claim 8 wherein the complexing agent is selected from at least on of the following classes of compounds: phosphates, phosphites, phosphines, phosphine oxides, phosphonates, diphosphonates, phosphinates, phosphinites, phosphonites, pyrophosphates, pyrophosphoramides, phosphor amides, phosphorothionates, phosphorodithionates, and phosphoramido thionates.

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